Applicable Standards:

* Product 🡪 99.5 (% minimum) Purity Propionic Acid with 0.1(% maximum) Water, Industrial Grade
  + Converted to Calcium, Ammonium, or Sodium salt for preserving feed and foodstuffs
  + Solvent for nitrate cellulose
* Quality Control:
  + Propionic Acid is only sold in pure form with a 99.5 wt % purity, determined acidimetrically. The maximum water content is 0.1 wt %; the sulfate, chloride, and heavy metal content is generally <1 ppm. The color index is normally below 5 APHA. Oxidizable substances (ketones, aldehydes, esters) can be determined from the reaction time in the KMnO4 test. Their proportions should be <0.05 wt %. The standard method for quality control is gas chromatography. Detection is carried out with a flame ionization detector (FID). The corresponding requirements are summarized below.

|  |  |  |
| --- | --- | --- |
| Specification | Limits | Analytical Method |
| **Propionic Acid Content, wt%** | **99.5** |  |
| **Water Content, wt%** | **0.1** |  |
| **Aldehydes, wt%** | **0.05** |  |
| **Readily Oxidizable Substances, wt%** | **0.05** |  |
| **Evaporation Residue, wt%** | **0.01** |  |
| **Iron, ppm (mg/kg)** | **1** |  |
| **Other heavy metals, ppm (mg/kg)** | **10** |  |
| **Platinum – cobalt color, APHA** | **10** |  |
| **Density (20oC), g/cm3** | **0.990-0.998** |  |
| **Bp, oC** | **140.7-141.6** |  |

* Shelf Life: 24 months for drums and 12 months for bulk
  + According to BASF, Propionic Acid has an almost unlimited shelf life in unopened, original containers and when properly stored in a protected storage area.
  + DOW States to attain maximum shelf life and preserve its quality, store under a nitrogen atmosphere and/ or use an appropriate desiccant system to prevent moisture contamination.
* Water Solubility: 37g/100 ml
* Piping Pressures
* Temperature/Pressure Controllers
* Flow meters
* Recovery systems
* Storage and Transportation:

Ordinary steel is totally unsuitable for the handling of Propionic Acid. Aluminum is only resistant at room temperature and to anhydrous, concentrated Propionic Acid; at higher temperature corrosiveness toward aluminum varies with the concentration of acid. Thus the corrosion maximum for 50 oC lies at 75% acid, whereas there are two maxima at the boiling point, a weaker one at 1% and a strong one at 99.8% acid. Copper and copper alloys are stable toward Propionic Acid up to its boiling point, but only if the solutions are free from air or oxidizing substances. Of the stainless steels, the ferritic chromium steels (13 – 17% Cr) are unsuitable because Propionic Acid tends to cause pitting. Generally, austenitic CrNi steels and CrNiMo steels are used for handling Propionic Acid. However, impurities in Propionic Acid can make the use of titanium or Hastelloy (e.g., Hastelloy C-22) equipment necessary, even below the boiling point. Above the boiling point, up to about 230 oC Hastelloy C-22 has shown excellent resistance even under oxidizing and reducing conditions. Above 230 oC only silver has proved to be a suitable material.

Containers made of aluminum with a purity of 99.5% or alloyed steels are suitable for storing pure Propionic Acid. Aluminum is unstable toward aqueous Propionic Acid. Polyethylene containers can be used for temporary storage of Propionic Acid and as small packing drums. Although, plastics are not recommended for long-term storage. Glass-reinforced plastics are unsuitable even for short-term storage.

* + HASTELLOY® C-22® alloy
    - Used to store the corrosive Propionic Acid, even at high enough temps

Competing Processes:

Industrially, Propionic Acid is currently produced almost exclusively by three different processes:

1) Carbonylation of ethylene with carbon monoxide and water

2) Oxidation of Propanal

3) Direct oxidation of hydrocarbons

The Koch synthesis has been investigated intensively. As a carbonylation reaction of ethylene in a strongly acidic medium, it is a variant of the Reppe synthesis. However, compared with the latter it never achieved much industrial significance and was carried out with little success.

Other possible sources of Propionic Acid, which are not used industrially for economic reasons, are its formation as a byproduct in the high- and low-pressure carbonylation of methanol to give acetic acid (2% formation of Propionic Acid), the direct reaction of ethylene, carbon monoxide, and water over noble-metal catalysts.

Two-step reactions have been described, in which Propionic Acid is obtained directly from synthesis gas (20 – 60 bar, 150 – 160 oC, Rh catalysts). With the current availability of ethylene and naphtha these processes are, however, not yet competitive. It is sometimes desirable, to use Propionic Acid produced by natural methods, particularly for the use of Propionic Acid in flavors and fragrances. Appropriate microbiological and enzymatic processes have been developed, which are usually based on the anaerobic fermentation of starch or sugars. However, the expensive production of this “natural” Propionic Acid limits its use to special areas of application.

**Carbonylation of Ethylene (BASF Process) (Our Old Process)**

In the Reppe synthesis ethylene is reacted with carbon monoxide and water in the presence of Ni(CO)4 (Nickel Carbonyl) according to the following process: the reaction takes place at high pressure and is characterized by low raw material costs, high conversion, high yield, and a simple workup. Ethylene and carbon monoxide are compressed and continuously pumped into the high-pressure reactor together with the feed solution. The crude Propionic Acid formed at 100 – 300 bar and 250 – 320 oC is drawn off at the head of the reactor and cooled in a heat exchanger with production of steam. Part of the cooled reaction product is recycled to the reactor for temperature regulation, the majority of it is allowed to expand and is separated into an off-gas and a crude acid stream. Nickel is recovered from the offgas and led back into the reactor. The off-gas is incinerated with recovery of heat. The crude acid stream is subsequently dehydrated and worked up by distillation in several following columns. The nickel salts that are formed are recycled into the process. The pure Propionic Acid is finally obtained by distillation. The product residue is channeled out of the process. Variants of the Reppe and Koch syntheses are possible, where the effect of inorganic salts on the reaction conditions and yield are important factors. Boric acid is reported to accelerate the reaction and hinder the precipitation of catalyst salts.

**Oxidation of Propanal (Our Process)**

The oxidation of propanal is an important route to Propionic Acid. This route is economically attractive although two steps (production of propanal and subsequent oxidation) are required: (1) Propanal is formed in large quantities as an intermediate in the production of npropanol by hydroformylation of ethylene, and (2) the oxidation takes place in plants in which other aliphatic carboxylic acids (n-butyric and isobutyric acids, n-valeric and isovaleric acids) are also produced. A high utilization of available capacity is therefore guaranteed in both steps.

**Propanal Production**

The production of propanal is carried out by the hydroformylation of ethylene. It is favored because, unlike the case of the higher aldehydes, n/isomixtures cannot be formed. Two syntheses compete: the classical cobalt- catalyzed high-pressure carbonylation at 200 – 280 bar, and 130 – 150 oC, and the rhodium- or iridium- catalyzed low-pressure carbonylation at about 20 bar, and about 100 oC. In the high-pressure synthesis the yield is generally impaired by partial hydrogenation of propanal to give propanol. The isolation of the aldehyde takes place, after removal of cobalt, by distillation of an azeotrope with ca. 98% aldehyde content. In the low-pressure synthesis (Union Carbide), the aldehyde can be distilled directly from the reaction mixture in 99% purity.

**Oxidation**

Propanal is subsequently oxidized under very mild conditions at 40 – 50 oC to Propionic Acid with high selectivity. In the United States Propionic Acid is produced by the oxidation of propanal by Union Carbide and Eastman Kodak.

**Direct Oxidation of Hydrocarbons**

A large quantity of Propionic Acid is obtained by the direct oxidation of hydrocarbons, predominantly naphtha. In this process, which is principally used for acetic acid production, formic acid, Propionic Acid, and an isomeric mixture of butyric acids are formed as byproducts. Whether this process is considered economic for Propionic Acid production is principally a question of the market evaluation of the different products. The process has favorable raw material costs, but requires a relatively complex workup of the product mixture. The composition of the acid mixture formed in the oxidation can be affected by the reaction conditions (pressure, temperature), the type of reactor (tubular reactor, column reactor), the raw material (naphtha, liquefied petroleum gas), and by the catalyst. If naphtha is used, the proportion of Propionic Acid in the mixture is about 10 – 15%. In other cases like with 2- methylpentane as a raw material, the proportion of Propionic Acid can increase to 31%. The total yield of acids does, however, vary considerably with the starting material.

**BP Chemicals Process**

Naphtha is preheated to 170 oC and oxidized with air at 40 – 45 bar in several reactors in series. Again, the heat of reaction is used for steam generation. The cooled discharge from the reactors is separated from the reaction off-gas in a separator. Entrained liquid is recovered from the off-gas and recycled to the reactor; the off-gas is then incinerated. The liquid reactor discharge is separated into an organic phase, which contains unreacted hydrocarbons, and an aqueous phase which contains the product mixture. The unreacted hydrocarbons are recycled to the reactor. The low- and high-boilers are separated from the aqueous phase which then gives the crude acid. From this the C1- to C4-acids are obtained by extractive dehydration followed by fractional distillation. Propionic Acid is produced by direct oxidation at BP Chemicals (UK), Hoechst – Celanese (United States), and Daicel (Japan).

* Hydrocarboxylation
  + Catalyst:
* Hydrocarbonylation
  + Catalyst:
* Wacker Process
  + Catalyst:
* Our Process:
  + Hydroformylation
    - Catalyst:
  + Oxidation of Aldehyde:
    - Catalyst